

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
25 July 2002 (25.07.2002)

PCT

(10) International Publication Number  
**WO 02/057536 A1**

- (51) International Patent Classification<sup>7</sup>: **D06P 1/44**, C09B 57/12 (74) Agent: **DÜNNWALD, Dieter**; Clariant International Ltd, Rothausstrasse 61, CH-4132 Muttenz 1 (CH).
- (21) International Application Number: PCT/IB02/00186 (81) Designated States (*national*): BR, CN, JP, KR, US.
- (22) International Filing Date: 21 January 2002 (21.01.2002) (84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR).
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 0101546.0 22 January 2001 (22.01.2001) GB
- (71) Applicant (*for all designated States except US*): **CLARIANT INTERNATIONAL LTD** [CH/CH]; Rothausstrasse 61, CH-4132 Muttenz 1 (CH).
- (72) Inventor; and
- (75) Inventor/Applicant (*for US only*): **SIEBER, Helmut** [DE/DE]; Füllenplatz 22, 79618 Rheinfelden (DE).

**Published:**  
— with international search report  
— entirely in electronic form (except for this front page) and available upon request from the International Bureau

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*



**WO 02/057536 A1**

(54) Title: USE OF PIGMENT DYES FOR DISPERSION DYEING FROM AQUEOUS MEDIA

(57) Abstract: Use of pigments according to formula (I) (formula see on enclosed paper version) wherein the substituents have the meanings as defined in claim 1 for dyeing semisynthetic or synthetic hydrophobic fiber materials in aqueous media as well as semisynthetic or synthetic hydrophobic fiber materials dyed with such pigments.

**USE OF PIGMENT DYES FOR DISPERSION DYEING FROM AQUEOUS MEDIA**

5 The invention relates to the use of certain pigments as disperse dyestuffs in aqueous media.

• The word "pigment" is of Latin origin (pigmentum) and originally denoted a color in the sense of a coloring matter, but was later extended to indicate colored decoration (e.g., makeup). In the late Middle Ages, the word was also used for all kinds of plant and vegetable extracts, especially those used for coloring. The word pigment is still used in this sense in biological terminology; it is taken to mean dyestuffs of plant or animal organisms that occur as very small grains inside the cells or cell membranes, as deposits in tissues, or suspended in body fluids.

15 The modern meaning associated with the word pigment originated in this century. According to accepted standards (DIN 55943 and DIN 55945) the word pigment means a substance consisting of small particles that is practically insoluble in the applied medium and is used on account of its coloring, protective, or magnetic properties. Both pigments and dyes are included in the general term "coloring materials", which denotes all materials used for their coloring properties. The characteristic that distinguishes pigments from soluble organic dyes is their low solubility in solvents and binders. Pigments can be characterized by their chemical composition, and by their optical or technical properties.

25 In the Color Index (C.I.) pigments are usually named "C.I. Pigment XY xy". Some compounds may be named "C.I. Solvent XY xy" due to their migration tendency in polymer application, although in water or organic solvents these compounds may fulfill the insolubility criteria for pigments, according to DIN 55943 and DIN 55945.

30 Pigments can be classified into two categories:

- (i) inorganic pigments
- (ii) organic pigments

35 The most important areas of use of pigments are paints, varnishes, plastics, artists' colors, printing inks for paper and textiles, leather decoration, building materials

(cement, renderings, concrete bricks and tiles - mostly based on iron oxide and chromium oxide pigments), leather imitates, floor coverings, rubber, paper, cosmetics, ceramic glazes, and enamels.

- 5    The paint industry uses high-quality pigments almost exclusively. An optimal, uniform particle size is important because it influences gloss, hiding power, tinting strength, and lightening power. Paint films must not be too thick, therefore pigments with good tinting strength and hiding power combined with optimum dispersing properties are needed.
- 10   White pigments are used for white coloring and covering, but also for reducing (lightening) colored and black pigments. They must have a minimal intrinsic color tone.

When choosing a pigment for a particular application, several points normally have to be considered. The coloring properties (e.g., color, tinting strength or lightening power, 15   hiding power) are important in determining application efficiency and hence economics. The following properties are also important:

- 1)    *General chemical and physical properties:* chemical composition, moisture and salt content, content of water-soluble and acid-soluble matter, particle size, 20   density, and hardness
- 2)    *Stability properties:* resistance toward light, weather, heat, and chemicals, anti-corrosive properties, retention of gloss
- 3)    *Behavior in binders:* interaction with the binder properties, dispersibility, special properties in certain binders, compatibility, and solidifying effect

25   One important field of application is the mass dyeing of polymer fibers, in particular polyester fibers. The process, wherein the polymer melt is directly dyed and spun is called "spin dyeing". The pigment dye is "dissolved" in the polymer melt, e.g. for polyester at temperatures above 260°C. For the melt spinning process the temperatures 30   are usually higher, e.g. for polyester at around 285°C. There are only few pigment classes which can resist these high temperatures without significant degradation of the dye molecule.

Disperse dyes are colorants with low water solubility that, in their disperse colloidal 35   form, are suitable for dyeing and printing hydrophobic fibers and fabrics.

Models for the dyeing of polyester fibers with disperse dyes have been developed. When the dye is applied from aqueous medium, it is adsorbed from the molecularly dispersed aqueous solution onto the fiber surface and then diffuses into the interior of the fiber. The following parameters determine the rate of dyeing and, to some extent, the leveling properties:

- (1) the dissolution rate during the transition from the dispersed crystalline state of the dye into the molecularly dispersed phase, and
- (2) the diffusion rate at the fiber surface and, especially, in the interior of the fiber.

10

The rates of both processes vary with temperature.

Differences in geometry and polarity of the dye molecules can lead to wide variations in these finishing or dye-specific properties and can have a marked effect on the absorption characteristics of all dyes, irrespective of whether single-component or combination dyeing processes are used. For instance, uneven dyeing may occur when an unequal distribution of particle size results in insufficient dispersion stability and, thus, crystal growth and precipitation at the substrate surface.

As the temperature in the dyeing process is usually below 120°C, the temperature stability of the dye molecules is not of great importance. In some cases the temperature in the dyeing process can be up to 130-140°C. Industrially applied disperse dyes are based on numerous chromophore systems. Approximately 60 % of all products are azo dyes and ca. 25 % are anthraquinone dyes, with the remainder distributed among quinophthalone, methine, naphthalimide, naphthoquinone, and nitro dyes. The dye molecules are usually modified by extensive substituents to optimize their properties according to the product to be dyed.

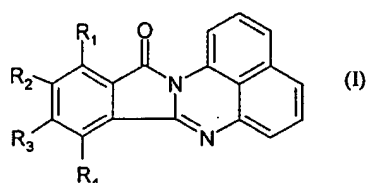
Surprisingly, it was found that certain pigments used for mass dyeing of polymer fibers, in particular polyester fibers (e.g. pigments of the trademarks Polysynthren® and Sandoplast® both Trademarks of CLARIANT) can be used for dyeing textile fibers in aqueous media.

There is a limited range of pigments, of very different chemical structure, used as dispersion dyes for mass dyeing of polyester. Common elements are that they have

rather symmetrical, compact and rigid structures with rather limited side groups, optimized in their stability at the high temperatures of the spin dying process.

Preferred examples for Polysynthren® and Sandoplast® pigments which can be used according to the invention are listed in the Color Index as C.I. Solvent Red 135 and C.I. Solvent Orange 60.

The invention related to the use of pigments or mixtures of pigments according to formula (I)



wherein  $R_1 - R_4$  independently from each other signify H, halogen,  $-NO_2$ ,  $-CN$ ,  $-OH$ ,  $-CH_3$ ,  $-NH_2$  or  $NHCH_3$ , in a dyeing process which takes place in aqueous media.

15 Preferably, pigments or mixtures of pigments are used wherein  $R_1 - R_4$  independently from each other signify H, halogen or  $-CN$ .

20 More preferably, pigments or mixtures of pigments are used wherein  $R_1 - R_4$  independently from each other signify H,  $-Cl$  or  $-CN$ .

Especially preferred are pigments of formula (I) or mixtures of pigments of formula (I) wherein all  $R_1 - R_4$  are either H or  $-Cl$ .

25 The pigment, wherein all  $R_1 - R_4$  of formula (I) are  $-Cl$ , is known as C.I. Solvent Red 135 (Polysynthren® Red GFP, Trademark of CLARIANT).

The pigment, wherein all  $R_1 - R_4$  of formula (I) are H, is known as C.I. Solvent Orange 60 (Sandoplast® Orange 3G, Trademark of NOVARTIS).

30 According to the invention, the pigments of formula (I) are used for dyeing and printing semisynthetic and, preferably, synthetic hydrophobic fiber materials, especially textile

materials. Textile materials consisting of blended fabrics containing such semisynthetic hydrophobic fiber materials can also be dyed or printed by means of the dyes of this invention.

- 5     Suitable semisynthetic textile materials are mainly cellulose-2½ acetate, cellulose triacetate polyamides and high molecular weight polyesters as well as mixtures thereof with cellulose.

- 10     Synthetic hydrophobic textile materials consist mainly of linear aromatic polyester, for example of those consisting of terephthalic acid and glycols, in particular ethylene glycol or condensate of terephthalic acid and 1,4-bis(hydroxymethyl)cyclohexane; of polycarbonates, e.g. those consisting of alpha,alpha-dimethyl-4,4'-dihydroxydiphenylmethane and phosgene, and of fibers based on polyvinyl chloride and polyamide.

- 15     The hydrophobic synthetic materials can be in the form of sheet-like or thread-like structures, and can be processed, for example, to yarns or woven, knitted or looped textile fabrics. The pigments of formula (I) are also suitable for dyeing hydrophobic synthetic material in the form of micro fibers.

- 20     It is expedient to convert the pigments according to formula (I) before use, into a dye formulation. This is done by milling the dye to an average particle size of 0.1 to 10 micron. Milling can be carried out in the presence of dispersants. Typically, the dried pigment is milled with a dispersant, and thereafter dried under vacuum or by spray drying. Printing pastes and dyebaths can be prepared by adding water to the formula-  
25     tion so obtained.

The pigments according to formula (I) are applied to the textile materials by known dyeing or printing methods, e.g. those described in French patent application No. 1445371.

30

Typically, polyester fiber materials are dyed from an aqueous dispersion by the exhaust process in the presence of customary anionic or non-ionic dispersants and in the presence or absence of customary swelling agents (carrier) in the temperature range from 65°C to 140°C.

35

Cellulose-2½-acetate is preferably dyed at a temperature from 65°C to 85°C and Cellulose triacetate at temperatures of up to 125°C.

The pigments according to formula (I) are suitable for dyeing by the thermosol process, for the exhaust and continuous process and for printing as for modern imaging processes, e.g. thermo-transfer printing or ink-jet printing.

The dyeings are carried out from an aqueous liquor by the exhaust process, and the liquor ratio can be chosen from a wide range, for example from 1:4 to 1:100, preferably from 1:6 to 1:50.

The dyeing time is from 20 to 90 minutes, preferably from 30 to 80 minutes.

The dye liquors can additionally comprise other additives, for example dyeing auxiliaries, dispersants, wetting agents and antifoams.

The liquor may also comprise mineral acids, such as sulfuric acid or phosphoric acid, or conveniently also organic acids, for example formic acid or acetic acid and/or salts, such as ammonium acetate or sodium sulfate. The acids mainly serve to adjust the pH of the dye liquors which is preferably in the range from 4 to 5.

The pigments are usually present in the dye liquors in the form of a fine dispersion. Suitable dispersants for the preparation of this dispersion are e.g. anionic dispersants, such as aromatic sulfonic acid/formaldehyde condensates, sulfonated creosol oil/-formaldehyde condensates, lignin sulfonates or copolymers of acrylic acid derivatives, preferably aromatic sulfonic acid/formaldehyde condensate or lignin sulfonated, or nonionic dispersants based on polyalkylene oxides obtainable, for examples, by polyaddition reaction from ethylene oxide or propylene oxide. Further suitable dispersants are listed in US 4,895,981 or US 5,910,624.

The dyeings or printings thus obtained, have good all-round fastness; particularly noticeable are the thermo-migration fastness, light fastness, thermo-fixation-, and pleating fastness, as well as the excellent wet fastness.

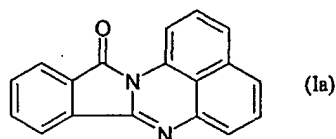
The invention further relates to semisynthetic or, preferably, synthetic hydrophobic fiber materials, which were dyed or printed with pigments of formula (I).

In the following examples, the parts and percentages are by weight. The temperatures are given in degrees Celsius.

5

**APPLICATION EXAMPLE**

17.5 parts of the pigment of the following formula (Ia)



10

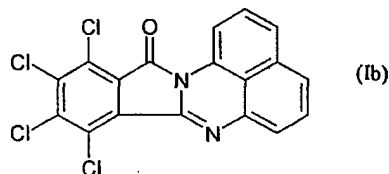
with 32.5 parts of a commercial dispersing agent based on lignin sulphonates, and pulverized to a powder. 1.2 parts of this dye preparation are added to 2000 parts of demineralized water of 70°C, which contains 40 parts of ammonium sulfate; the pH value of the dye bath is set at 5 with 85% formic acid. 100 parts of washed polyester fiber fabric are placed in this dye bath, the container is closed, heated to 130°C over the course of 20 minutes, and dyeing continues for a further 60 minutes at this temperature. After cooling, the polyester fiber fabric is removed from the dye bath, rinsed, soaped and cleansed by reduction with sodium hydrosulphite in the usual way. After thermo-fixation (180°C, 30 min), a orange dyeing is obtained with very good all-round fastness, especially fastness to light and sublimation, in particular excellent wet fastness.

15

20

Dyeing polyester yarn can be carried out analogously with the pigment according to the following formula (Ib)

25



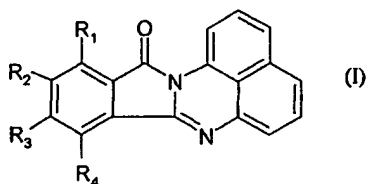
A red dyeing is obtained.



**PATENT CLAIMS**

1. Use of pigments or mixtures of pigments according to formula (I)

5



wherein  $R_1 - R_4$  independently from each other signify H, halogen,  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $-\text{OH}$ ,  $-\text{CH}_3$ ,  $-\text{NH}_2$  or  $\text{NHCH}_3$ , for dyeing semisynthetic or synthetic hydrophobic fiber materials characterized in that the dyeing process takes place in an aqueous media.

10

2. Use of a pigment according to claim 1 wherein  $R_1 - R_4$  independently from each other signify H, halogen or  $-\text{CN}$ .
3. Use of a pigment according to claim 1 wherein  $R_1 - R_4$  independently from each other signify H,  $-\text{Cl}$  or  $-\text{CN}$ .
4. Use of a pigment according to claim 1 wherein all  $R_1 - R_4$  are H.
5. Semisynthetic or synthetic hydrophobic fiber materials dyed in using pigments according to anyone of claims 1 to 4.

25

## INTERNATIONAL SEARCH REPORT

Int. Application No.

PCT/IB 02/00186

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 D06P1/44 C09B57/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
 IPC 7 D06P C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 20 09 465 A (BASF AG) 9 September 1971 (1971-09-09) the whole document	5
X	US 5 830 931 A (KALZ DIETMAR ET AL) 3 November 1998 (1998-11-03) examples 1,2 column 4, line 23 - line 36	5
A	US 3 676 051 A (KANGLE PURUSHOTTAM JANARDAN ET AL) 11 July 1972 (1972-07-11) column 1, line 31 - line 33 column 4, line 28 - line 59 column 5, line 69	1-5
A	GB 1 081 525 A (HOECHST AG) 31 August 1967 (1967-08-31) the whole document	1-5
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*Z\* document member of the same patent family

Date of the actual completion of the international search

25 April 2002

Date of mailing of the international search report

06/05/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Fiocco, M

## INTERNATIONAL SEARCH REPORT

Int'l Application No

PCT/IB 02/00186

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 095 035 A (BASF AG) 13 December 1967 (1967-12-13) page 1, line 15 - line 25 page 2, line 29 - line 32 -----	1-5

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

## INTERNATIONAL SEARCH REPORT

Int: Application No

PCT/IB 02/00186

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 2009465	A	09-09-1971	DE 2009465 A1	09-09-1971
US 5830931	A	03-11-1998	DE 19548453 A1	26-06-1997
			DE 59607629 D1	11-10-2001
			EP 0780444 A2	25-06-1997
			JP 9227789 A	02-09-1997
US 3676051	A	11-07-1972	CH 544842 B	13-07-1973
			CH 915869 A	13-07-1973
			DE 2027952 A1	23-12-1970
			ES 380762 A1	01-04-1973
			FR 2046788 A5	12-03-1971
			GB 1286719 A	23-08-1972
			JP 49042865 B	18-11-1974
			NL 7008727 A	18-12-1970
			ZA 7003998 A	24-02-1971
GB 1081525	A	31-08-1967	CH 432459 B	15-09-1966
			CH 364765 A	
			FR 1428752 A	18-02-1966
			US 3399026 A	27-08-1968
GB 1095035	A	13-12-1967	DE 1282214 B	07-11-1968
			DE 1296290 B	29-05-1969
			BE 662563 A	15-10-1965
			CH 482797 A	15-12-1969
			FR 1430705 A	04-03-1966
			US 3342818 A	19-09-1967